

PATENT SPECIFICATION

1,161,072

NO DRAWINGS.

1,161,072



Date of Application (No. 36644/66) and filing Complete Specification: 16 Aug., 1966.

Application made in United States of America (No. 485,538) on 7 Sept., 1965.

Complete Specification Published: 13 Aug., 1969.

Index at Acceptance:—C3 P(4A, 4D3B1, 4D3B3, 4D8, 4K8, 4K11, 4P1E1, 4P1E5, 4P2A2, 4P2A3, 4P2A4, 4P2A5, 7A, 7D1A, 7D1C, 7D2A1, 7D2A2B, 7D2A4, 7D3, 7K11, 7P1E5, 7P2A2, 7P2A3, 7P2A4, 7P2A5, 7P2X, 8A, 8C4A, 8C8B, 8C9, 8C10, 8C13A, 8C14A, 8C14B, 8C20B, 8D1A, 8D2A, 8D2B2, 8D3A, 8D4, 8D5, 8D8, 8K4, 8K8, 8K11, 8P1D, 8P1E1, 8P1E2, 8P1E5, 8P2A3, 8P2A4, 8P2A5, 8P2C, 9A, 9D1B3, 9D3, 9K11, 9P1E5, 9P2A2, 9P2A3, 9P2A4, 9P2A5, 10A, 10D1A, 10D2A, 10K11, 10P1E5, 10P2A2, 10P2A3, 10P2A4, 10P2A5, 11A, 11C4A, 11C8B, 11C9, 11C10, 11C13A, 11C14A, 11C14B, 11C20B, 11D4, 11D8, 11K4, 11K7, 11K8, 11K9, 11K10, 11K11, 11P1D, 11P1E1, 11P1E2, 11P1E5, 11P2A2, 11P2A3, 11P2A4, 11P2A5, 11P2C, 11P2X); B2 K(6A, 7AY, 8D, 9C, 9J, 9QY, 9Q2, 9Q6, 9Q7, 9Q12, 9QX).

International Classification:—C 08 f 21/00.

COMPLETE SPECIFICATION.

Preparation of Co-Polymers.

We, DOW CORNING CORPORATION, of Midland, Michigan, United States of America, a corporation organised under the laws of the State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for preparing siloxane-organic co-polymers and to the co-polymers made by the process of this invention.

This invention provides a process for preparing a polysiloxane-organic co-polymer which comprises (1) preparing an emulsion of a polysiloxane containing a substituent containing an ethylenic double bond, (2) adding at least one olefinically unsaturated organic monomer to the polysiloxane emulsion, and (3) thereafter co-polymerising the polysiloxane and the organic monomer.

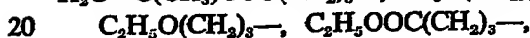
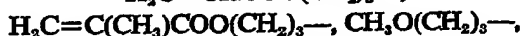
The first essential phase of the process of this invention involves the preparation of an emulsion of a polysiloxane containing a vinylidene substituent. This can be done in a number of ways. For example, a sil-

oxane polymer can be prepared by any of the conventional techniques and then mixed with water and a surfactant and emulsified by shaking or on a homogeniser. Another way would be to polymerise cyclic siloxanes employing the emulsion polymerisation techniques set forth in Specification No. 785,174. Still another method is to emulsion polymerise a siloxane starting with an alkoxy-silane employing the techniques set forth in our co-pending Application No. 13903/64 (Serial No. 1,024,024). The preferred method is one of the emulsion polymerisation techniques, especially starting with the appropriate alkoxy-silanes and using ammonium hydroxide as the catalyst.

According to a modification of the process of the invention, the organic monomer is emulsified together with the polysiloxane.

The siloxane units making up the siloxane polymer can have the unit formulae $R_nSiO_{n/2}$, R_nSiO and/or $RSiO_{1/2}$. Of course the polymer can be either a homo-polymer or a co-polymer, and in the latter case small amounts of SiO_2 units can also be present. The R substituents can be either hydrocarbon or substituted hydrocarbon radicals.

Thus R can be an alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl alkaryl or an aralkyl radical; the halogenated derivatives of the foregoing hydrocarbon radicals; cyano-substituted hydrocarbon radicals; or radicals containing ether, thioether, ester or thioester linkages. By way of illustration, R can be a methyl, ethyl, propyl, butyl, amyl, dodecyl, octadecyl, myricyl, vinyl, allyl, hexenyl, ethynyl, propargyl, cyclobutyl, cyclohexyl, cyclohexenyl, phenyl, naphthyl, xenyl, tolyl, xylyl, mesityl, tertiary-butylphenyl, benzyl, 2-phenylethyl, 2-phenylpropyl, 3-chloropropyl, 3,3,3-trifluoropropyl, perfluorovinyl, chlorocyclohexyl, bromophenyl, dichlorophenyl, α,α,α -trifluorotolyl, delta-cyanobutyl omega-cyano-octadecyl,



or a $\text{C}_6\text{H}_5\text{S}(\text{CH}_2)_3-$ radical. Preferred R groups are those containing from 1 to 18 carbon atoms with the methyl, ethyl, vinyl, phenyl and 3,3,3-trifluoropropyl radicals as the most preferred substituents. It is essential that at least some of the R groups in the siloxane are vinylic in order to form a copolymer with the organic monomer. Of course, small amounts of SiO_2 units can also be present in co-polymer.

Any olefinically unsaturated organic monomer or mixture of such monomers can be co-polymerised with the polysiloxane. Organic monomers are well-known materials, are readily available, and are defined as having at least one polymerisable unsaturated carbon-to-carbon bond in each molecule. Examples of such materials include vinyl-, vinylidene- and allyl-aromatic compounds such as styrene, the vinyl toluenes, the methyl styrenes, the ethyl styrenes, the propyl styrenes, the vinyl diphenyls, the vinyl diphenyl ethers of the vinyl naphthalenes, the substituted vinyl-, allyl- and vinylidene-aromatics including the alkyl, phenyl, alkoxy, phenoxy, acetyl, acylamino, isocyanate, carbamide, amido, amino, nitrile, carbonylamido, trifluoromethyl, phosphoro, and halogeno (F, Cl, Br) substituents including the mono-, di-, tri- and tetra- substituted styrenes, methyl styrenes, ethyl styrenes, and isopropyl styrenes; esters of olefinic acids including α and β substituted olefinic acids for example the acrylates and including alkyl, cycloalkyl, alkenyl, aryl, aralkyl esters such as the methyl, ethyl, propyl, butyl, isobutyl, pentyl, hexyl, cyclohexyl, phenyl esters of

acrylic, methacrylic, and ethacrylic acids and including the α -haloacrylates such as methyl α -chloroacrylate, and propyl α -chloroacrylate; the esters of olefinic alcohols with saturated acids, such as the allyl, methallyl, crotyl, 1-chloroallyl, 2-chloroallyl, vinyl, or methylvinyl, esters of saturated aliphatic and aromatic monobasic acids such as vinyl and allyl acetate, isopropenyl acetate, vinyl formate, vinyl 2-ethylhexoate, methyl vinyl acetate, vinyl and allyl propionate, vinyl and allyl benzoate, the vinyl alkyl esters of olefinic dicarboxylic acids such as the vinyl alkyl esters from such alkyl radicals as methyl, ethyl, propyl, and the like up to C_{18} , of the olefinic dicarboxylic acids including maleic, citraconic, itaconic, muconic, glutaric, fumaric and derivatives of these esters such as vinyl ethyl-chloromaleate olefinic acid esters of epoxy alcohols, such as 2,3-epoxypropyl methacrylate or acrylate, glycidyl methacrylate, glycidyl acrylate, glycidyl crotonate, benzene vinyl monoepoxide and the reaction products of such with amines, such as trimethyl amide; the olefinic halides, such as vinyl fluoride, vinyl chloride, vinyl bromide, vinylidene fluoride and vinylidene chloride; the alkenyl ketones such as methyl vinyl ketone and isopropenyl methyl ketone; the olefinic ethers such as vinyl ethyl ether, vinyl butyl ether, vinyl cyclohexyl ether, vinyl phenyl ether, vinyl tolyl ether and vinyl benzyl ether; the olefinic aldehydes such as acrolein, and methacrolein; the amino olefinic ethers such as the amino vinyl ethers including aminoethylvinyl ether, aminopropylvinyl ether, N-methylaminoethylvinyl ether, and N,N-diethylaminoethylvinyl ether; nitrogen containing esters of olefinic acids such as aminocyclohexyl methacrylate, triethanolamine monomethacrylate, β -piperidyl-N-ethyl methacrylate, β -morpholine-N-ethyl methacrylate, N-methacrylyl morpholine, N-methacrylyl thiomorpholine, N-methacrylyl piperidines, N-acrylyl morpholine, N-acrylyl thiomorpholine and N-acrylyl piperidine the quaternary ammonium monomers, including methacryloxyethyltrimethylammonium methylsulphate and various quaternising reaction products of quaternising agents such as alkyl halides, alkyl sulphonates and alkyl phosphates (e.g. methyl bromide and toluene sulphonate) with tertiary amine monomers such as β -dimethylaminoethyl methacrylate, methyl- α -diethyl aminoacrylate, methyl α -(N)-methyl-anilino-acrylate, methyl α -dibenzylaminoacrylate and methyl α -distearyl amino acrylate; the monoolefinic triazine monomers including triazine monomers in which one of the carbons of the triazine ring is attached to a vinyl, and allyl radical and the other carbons of the triazine are attached to cyano, halo (F, Cl, Br), amino, alkoxy, cycloaliphatic (e.g. cyclopentyl, cyclohexyl) aro-

1,161,072

3

- matic-substituted (e.g. phenyl, biphenyl, naphthyl) alkylaryl (e.g. tolyl, xylyl, ethylphenyl) halogenated aromatic; the N-vinyl-N-alkyl-guanidines such as N-vinyl-N-butylguanidine, N-vinyl-N-benzyl guanidine, acryloguanamine and methacryloguanamine, the N-vinyl monomers such as N-vinylpyrrole, N-vinyl carbazole, N-vinylindole and N-vinyl succinimide N-vinyl lactams such as N-vinyl caprolactams and N-vinyl butyrolactum the amides and substituted amides of acrylic acid and α - and β - substituted acrylic acids such as acrylamide, methacrylamide, ethacrylamide, N-methacrylamide, N-methylmethacrylamide, N,N-bis(hydroxyethyl)acrylamide, N,N-diethylacrylamide, N,N-ethylmethacrylamide and other mono- and di-N-substituted unsaturated acid amides where the substituents is a alkyl radical containing from 1 to 5 carbon atoms alkoxy, haloalkyl; the olefinic nitriles such as acrylonitrile, methacrylonitrile, ethacrylonitrile and chloroacrylonitrile; the fluoro-substituted nitriles of olefinic acids such as N-(2,2,3-trifluoroethyl) acrylamide, methacrylamide, N-(2,2-difluoroethyl)acrylamide and methacrylamide; the acylamino substituted acrylic and α - and β -acrylic acid esters such as the methyl, ethyl and propyl alkyl esters of α -acetoaminoacrylate, and α -N-butylaminoacrylate; the vinyl pyridines such as 2-vinyl pyridine, 3-vinylpyridine, 4-vinylpyridine, 2-vinyl-5-ethyl pyridine, 2-methyl-5-vinylpyridine and the other ethyl and methyl isomers of vinylpyridine; the vinyl heterocyclic compounds such as 2-vinylfuran and 2-vinylthiophene; the phosphorus containing monomers such as acrylic esters containing phosphonamido groups such as diamidophosphoroacrylate and other similar polymerisable materials having a polymerisable unsaturated carbon-to-carbon bond.
- The conjugated dienes include the following: hydrocarbon conjugated dienes such as butadiene-1,3, isoprene, 2,3-dimethylbutadiene-1,4, piperylene, pentadiene-1,3, and 2 phenyl butadiene-1,3; the polar conjugated dienes such as 1- and 2-cyano-butadiene-1,3 and 2-chlorobutadiene-1,3.
- Monomer materials having a plurality of polymerisable unsaturated carbon-to-carbon bonds at least two of which are non-conjugated, including the polyunsaturated esters of olefinic alcohols and unsaturated monocarboxylic acids such as the vinyl, vinylidene, and allyl esters of unsaturated monocarboxylic acids such as vinyl acrylate, allyl acrylate, the vinyl and allyl esters of α - and β - substituted acrylates such as vinyl methacrylate, vinyl crotonate, vinyl ethacrylate, allyl methacrylate, allyl ethacrylate, vinyl α -chloroacrylate, and allyl α -hydroxyethyl acrylate, the polyunsaturated esters of saturated dicarboxylic and polycarboxylic acids such as the vinyl, vinylidene, allyl esters and mixed esters of such dicarboxylic acids as oxalic, malonic, succinic, glutaric, adipic, tartaric and citric acids, polyunsaturated esters of unsaturated polycarboxylic acids, such as the vinyl, vinylidene, and allyl esters and mixed esters of the unsaturated polycarboxylic acids such as maleic, citraconic, itaconic, mesaconic, fumaric, muconic, chloromaleic and aconitic acids including such monomers as diallyl fumarate, diallyl homophthalate, diallyl itaconic, diallyl ester of muconic acid, diallyl maleate, diallyl phthalate, diallyl isophthalate, and diallyl terephthalate, polyhydroxy esters of unsaturated acids such as the glycol esters, glycol ether esters, the trihydroxy-, tetrahydroxy-, pentahydroxy-, hexahydroxy- esters including the glycerides, the pentoses, the hexose esters of acrylic acid and α - and β -substituted acrylic acid such as ethylene diacrylate, ethylene dimethacrylate, propylene dimethacrylate, glycerol dimethacrylate, glyceryl trimethacrylate, tetramethylene diacrylate and dimethacrylate and tetraethylene glycol dimethacrylate; polyunsaturated acid amides such as N,N-diallyl acrylamide, N,N-diallyl methacrylamide and N,N-methylene bisacrylamide; polyunsaturated ethers such as divinyl ether, diallyl ether, divinyl carbitol and divinyl ether of diethylene glycol polyunsaturated triazines, the diallyl cyanurates, triallyl cyanurate, the di- and tri- vinyl cyanurates and derivatives of these; the polyalkene aryl compounds and derivatives including the polyvinyl-, polyvinylidene- and polyallyl aryl compounds, such as divinyl benzene, trivinyl benzene, divinyl toluene, trivinyl toluene, divinyl xylene, divinyl ethyl benzene, divinyl biphenyl and divinyl biphenyl oxide, divinyl naphthalenes, divinyl methylnaphthalenes, and derivatives of these including those with alkyl, alkoxy, phenoxy, acetyl, isocyno, amino, nitrile, trifluoro methyl, and halo (F, Cl, Br) substituents; and other monomers containing a plurality of vinyl, vinylidene, allyl, alkenyl and other polymerisable unsaturated double and triple bonds.
- The co-polymerisation of the polysiloxane and organic monomer can be achieved by any suitable means such as light, heat, pressure, radiation, catalysis or a combination of these. In the process of this invention it is generally preferred to employ a free radical catalyst to promote the co-polymerisation. It is generally understood by those skilled in the art that the co-polymerisation is achieved by activation of the unsaturated bonds in the co-reactants. Examples of suitable catalysts include the inorganic peroxides such as hydrogen peroxide; the various organic peroxy catalysts, such as the dialkyl peroxides, e.g. diethyl peroxide, diisopropyl peroxide, dilauryl peroxide, dioleoyl peroxide, distearyl peroxide, di-(tertiary-butyl) per-

oxide; di- (tertiary amyl) peroxide and dicumyl peroxide; the alkyl hydrogen peroxides such as tertiary butyl hydroperoxide, tertiary amyl hydroperoxide, cumene hydroperoxide, tetralin hydroperoxide, and diisopropylbenzene hydroperoxide; the symmetrical diacyl peroxides, for instance acetyl peroxide, propionyl peroxide, lauroyl peroxide, stearoyl peroxide, amlonyl peroxide, succinoyl peroxide, phthaloyl peroxide, benzoyl peroxide; ketone peroxides such as methylethyl ketone peroxide and cyclohexanone peroxide, the fatty oil acid peroxides, such as coconut oil acid peroxides; the unsymmetrical or mixed diacyl peroxides, such as acetyl benzoyl peroxide and propionyl benzoyl peroxide the azo compounds such as 2-azobis(isobutyronitrile), 2-azobis(2-methylbutyronitrile) and 1-azobis(1-cyclohexanecarbonitrile) and other free radical generating catalysts such as the disulphides are useful herein.

The addition of the organic monomer to the siloxane emulsion can be done in several ways. For example, all the monomer to be co-polymerised can be added at one time or, alternatively, the monomer can be added continuously or incrementally over a period of time. Also, a quantity of the monomer can be added initially with the balance of the monomer being added continuously or incrementally over a period of time.

When a catalyst is used to promote the co-polymerisation, it can be added to the siloxane emulsion in any of the ways set forth above for the organic monomer.

While the co-polymerisation will generally take place at room temperature, in order to get a reasonable reaction rate it is desirable to heat the mixture in the range of 50° to 90°C. Of course, the mixture is agitated while the polymerisation is being carried out and in some instances it may be desirable to carry out the reaction under an inert atmosphere.

The following examples illustrate the invention. All percents are by weight unless otherwise specified.

Example 1

160 G. of vinylmethylcyclotetrasiloxane, 40 g. of styrene, 350 g. of water and 12 g. of a 50% active aqueous solution of tallowtrimethyl ammonium chloride were emulsified in a commercial mixer. To the resulting emulsion 10 ml. of concentrated ammonium hydroxide was added and the emulsion was placed in a 90°C. oven. After four hours, 0.5 g. of potassium persulphate in 50 g. of water was added to the emulsion and it was returned to the oven for sixteen and one-half hours. At the end of this time the emulsion was removed from the oven. The emulsion was opalescent in appearance.

A small sample of the emulsion was

placed in a glass dish which was put in the oven and the volatiles constituents evaporated. The siloxane-styrene co-polymer obtained was a greasy wax. The balance of the co-polymer was obtained from the remainder of the emulsion by removing the volatiles constituents on a drum drier, and the copolymer solids were dried for two hours in the oven.

Example 2

109.4 G. of styrene, 90.4 g. of vinylmethylcyclotetrasiloxane, 12 g. of a 50% active aqueous solution of tallowtrimethyl ammonium chloride and 350 g. of water were emulsified on a commercial mixer. 10 ml. of concentrated ammonium hydroxide were added to the resulting emulsion and it was then placed in a 90°C. oven for three hours. 0.5 G. of potassium persulphate in 50 g. of water was added to the emulsion and it was placed in a 70°C. oven for eighteen hours. After this time, the emulsion was removed from the oven and the siloxane-styrene co-polymer recovered therefrom as an extremely fine powder by evaporating the volatile constituents on a drum drier.

Example 3

85 G. of styrene, 15 g. of vinylmethylcyclotetrasiloxane, 2 g. of sodium dodecylbenzene sulphonate, 1 g. of dodecylbenzene sulphonic acid and 200 g. of water were emulsified and then the emulsion placed in a 70°C. oven for seventeen hours. 0.6 G. of potassium persulphate in water solution was then added to the emulsion and it was returned to the oven for three and one-half hours after which time the siloxane and styrene had essentially completely copolymerised.

Example 4

The procedure of Example 3 was repeated using 170 g. of styrene, 30 g. of vinylmethylcyclotetrasiloxane, 4 g. of sodium dodecylbenzene sulphonate, 2 g. of dodecyl benzene sulphonic acid and 224 g. of water. Identical results were obtained. The emulsion was adjusted to 35.7% co-polymer solids by removing volatile constituents at 150°C. A film of the co-polymer cast from this emulsion was brittle and non-continuous.

Example 5

120 G. of styrene, 30 g. of vinylmethylcyclotetrasiloxane, 50 g. of dimethylcyclotetrasiloxane, 4 g. of sodium dodecylbenzene sulphonate, 2 g. of dodecylbenzene sulphonic acid and 224 g. of water were emulsified and placed in a 70°C. oven for two hours to polymerise the siloxanes. The emulsion was removed from the oven and allowed to stand at room temperature for 24 hours. Then 0.5 g. of potassium persulphate was added to the

1,161,072

5

emulsion and it was returned to the oven for sixteen and one-half hours for co-polymerisation of the siloxane and styrene.

Example 6

- 5 Each of the nine formulations composed of varying amounts of styrene, vinylmethylcyclotetrasiloxane and dimethylcyclotetrasiloxane, and identified as A to I inclusive below, were added to 208 g. of water having 2 g. of sodium dodecylbenzene sulphonate and 1g. of dodecyl benzene sulphonic

acid dissolved therein and then emulsified on a homogeniser at 281.2 kg/sq.cm. The emulsions were placed in a 70°C. oven for four and one-half hours to polymerise the siloxanes. Then to 50 g. samples of each of these emulsions there was added 10 g. of water having 0.1 g. of potassium persulphate dissolved therein. These samples were then returned to the oven for about 19 hours for the silicone-organic co-polymerisation. The formulation quantities in grams is set forth in the table below.

| | Formulation | Styrene | (ViMeSiO) ₄ | (Me ₂ SiO) ₄ |
|----|-------------|---------|------------------------|------------------------------------|
| 25 | A ... | 40 | 12 | 48 |
| | B ... | 40 | 18 | 42 |
| | C ... | 40 | 24 | 36 |
| | D ... | 55 | 9 | 36 |
| | E ... | 55 | 13.5 | 31.5 |
| 30 | F ... | 55 | 18 | 27 |
| | G ... | 70 | 6 | 24 |
| | H ... | 70 | 9 | 21 |
| | I ... | 70 | 12 | 18 |

- 35 Samples of the silicone-styrene co-polymer emulsions were placed in aluminium cups and the volatile constituents allowed to evaporate at room temperature. The copolymer films left in the cups were examined and found to have the following characteristics. Formulations A to F inclusive all resulted in rubbery films whereas formulations G to I inclusive resulted in resinous films. The films from A and G to I inclusive were non-continuous whereas the films from B to F inclusive were continuous. Also, the films from A to C inclusive were all tacky.
- 40 The foregoing example shows that by varying the different portions of the copolymer one can obtain whatever properties are desired in the final product.

three drops per twenty seconds until it was all added, heating and agitation being maintained for about seventeen and one-half hours. The emulsion was broken with isopropanol and the siloxane-styrene copolymer solids filtered, and washed several times with hot water. About 100 g. of the washed copolymer solids were dried on a heated two roll mill. The co-polymer was gum-like while on the mill but became brittle upon cooling.

Example 8

When the process of the receding examples was repeated except that the organic monomers listed below were substituted for the styrene in equivalent amounts, silicone-organic co-polymers were obtained. In the case of the ethylene and propylene, the gases were bubbled into the emulsion.

| | |
|---------------------|-----|
| Acrylonitrile | |
| Vinyl acetate | |
| Ethylene | |
| Propylene | |
| Methylstyrene | 95 |
| Vinyl chloride | |
| Vinylidene chloride | |
| Divinyl toluene | |
| Diallyl itaconate | |
| Methacrylamide. | 100 |

Example 7

- 36 G. of a 50% active aqueous solution of tallowtrimethyl ammonium chloride, and 0.3 g. of sodium carbonate were dissolved in 600 g. of water and then 140 g. of styrene, 180 g. of phenylmethylcyclotetrasiloxane and 30 g. of vinylmethylcyclotetrasiloxane were added thereto. The resulting mixture was emulsified in a homogeniser at 281.2 kg/sq. cm.

- 60 The above emulsion was placed in a two litre, three-necked flask equipped with a stirrer, reflux condenser and an automatic temperature control which was set at 70°C. After one-half hour 12 ml. of aqueous sodium hydroxide, containing about 0.14 g. of sodium hydroxide, was added and the mixture agitated at 70°C. for another half hour. Next, 100 g. of water having 2 g. of potassium persulphate dissolved therein was added to the emulsion at the rate of about

Example 9

254.4 G of distilled water, 6 g. of sodium dodecylbenzene sulphonate and 4 g. of reagent grade (28%) ammonium hydroxide were placed in a 500 ml. beaker and heated to 65°C. while agitating with an electric stirrer. Then a mixture of 10g. of vinyltrimethoxysilane, 90.4 g. of phenylmethyldi-

methoxysilane and 50 g. of phenyltrimethoxysilane was added to the beaker via a dropping funnel over 10 minutes. After the silane addition was complete, agitation and heating was continued for another 10 minutes. 300 G. of the resulting opalescent emulsion was heated to boiling (86°–90°C.) and about 70 ml. of volatile constituents distilled off (primarily methanol and ammonia) leaving a siloxane emulsion having about 30% solids and a pH in the range of 7.5 to 8.0.

190 G. of the above siloxane emulsion, 6.4 g. of an anionic surfactant solution (36% solids) and a mixture of 34 g. of distilled water and 0.95 g. of acrylic acid were placed in a beaker and the pH adjusted to 5.0 by adding 3 g. of a 7% sodium bicarbonate solution. This mixture was placed in a three-necked flask, purged with nitrogen, heated to 85°C., then 10% of a mixture of 79.8 g. of ethylacrylate and 53.2 g. of methyl methacrylate was added, and next 25% of a solution of 34.7 g. of distilled water and 0.76 g. of potassium persulphate was added. Over the next 45 minutes, the balance of the acrylate and persulphate solution was added, the balance of the persulphate being added in three (25%) increments when 25, 50 and 75% of the remaining acrylate had been added. Of course, the reaction temperature was maintained at 85°C. and the nitrogen purge and agitation were maintained throughout the reaction. After the reaction was complete, the emulsion of the siloxane-acrylate co-polymer was cooled, the pH adjusted to 8.6 with ammonium hydroxide, and 20 g. of distilled water added to adjust the viscosity to 262 cps.

A film of the co-polymer was cast from the above emulsion onto a metal panel. Wetting of the panel by the emulsion was excellent and the resulting co-polymer film completely clear. The film had a pencil hardness of B and excellent flexibility.

Example 10

A mixture of 677.6 g. of distilled water, 11 g. of ammonium hydroxide, 14 g. of an adduct of 1 mol of nonylphenol with nine mols of ethylene oxide and 40.2 g. of an anionic surfactant were placed in a beaker and heated to 60°C. A mixture of 41.8 g. of methyltrimethoxysilane, 214 g. of phenyltrimethoxysilane, 51 g. of diphenyldimethoxysilane, 148 g. of dimethyldimethoxysilane and 22.5 g. of vinyltrimethoxysilane was added with constant stirring over a period of 10 minutes. After the addition was complete, the mixture was held at 60°C. with agitation for about 30 minutes, and then 280 ml. of volatile constituents were distilled off.

154 G. of the above siloxane emulsion was mixed with 1.27 g. of acrylic acid, 3.24 g.

of sodium dodecylbenzene sulphonate and 80.77 g. of water and the pH of the resulting mixture adjusted to 5 by adding about 4 g. of a 7% sodium bicarbonate solution. To this was added a mixture of 75.5 g. of ethyl acrylate and 50.5 g. of methylmethacrylate and a solution of 30 g. of water and 0.72 g. of potassium persulphate, these mixtures being added as in the previous examples with the reaction being complete after about one hour. The product was an emulsion of the siloxane-acrylate co-polymer. The co-polymer was thermoplastic when hot. A film of the co-polymer was cast on a metal panel and cured for 15 minutes at 150°C. It had a pencil hardness of HB and excellent flexibility. Another film of the co-polymer which had been cured for 15 minutes at 205°C. had a pencil hardness of 3H and excellent flexibility.

Example 11

To 372 g. of a aqueous emulsion of a siloxane co-polymer composed of 95 mol per cent diphenylsiloxane units and 5 mol per cent monovinylsiloxane units, there being about 35% of siloxane solids in the emulsion, there was added 2.7 g. of acrylic acid, 6.9 g. of sodium dodecylbenzene sulphonate and 173 g. of water, and then the pH was adjusted to 5 by adding about 13 g. of a 7% sodium bicarbonate solution. The resulting mixture was heated to 85°C. and a mixture of 160 g. of ethyl acrylate and 107 g. of methyl methacrylate was added. A solution of 63.5 g. of water and 1.5 g. of potassium persulphate was then added as in the previous examples with the reaction being completed in about 45 minutes. The product was an emulsion of the siloxane-acrylate co-polymer. A 10 mil draw-down was made on a metal panel and the resulting co-polymer film cured 5 minutes at 150°C. Wetting of the panel by the emulsion was excellent and the resulting film was transparent. The film had a pencil hardness of B and excellent flexibility.

A pigment dispersion was made by mixing 1000 g. of water, 31.6 g. of an anionic surfactant, 815 g. of titanium dioxide, 136 g. of mica, 454 g. of calcium carbonate, 204 g. of aluminium silicate, 68 g. of ethylene glycol, 9.1 g. of 1200 molecular weight polyethylene glycol and 18.1 g. of 4000 cps methyl cellulose, the latter three ingredients having been premixed. This mixture was then tinted to the desired shade of green with yellow iron oxide and phthalo green. 100 G. of this pigment dispersion was thoroughly mixed with 100 g. of the emulsion of the siloxane-acrylate co-polymer prepared above and the resulting latex paint coated on a metal panel. The wetting was excellent and upon drying the paint film,

had a pencil hardness of B and excellent flexibility.

Example 12

To 1350 g. of an aqueous emulsion of a siloxane co-polymer composed of 10 mol per cent of monomethylsiloxane units, 35 mol per cent of monophenylsiloxane units, 5 mol per cent of monovinylsiloxane units, 10 mol per cent of diphenylsiloxane units and 40 mol per cent of dimethylsiloxane units, there being about 40% of siloxane solids in the emulsion, there was added 970 g. of water, 10 g. of acrylic acid and 31.5 g. of an anionic surfactant. The mixture was heated to about 85°C. and next a mixture of 755 g. of ethyl acrylate, 480 g. of methylmethacrylate, 25 g. of hydroxypropyl methacrylate and 26.7 g. of acrylic acid was added along with a solution of 300 g. of water and 5 g. of potassium persulphate, these mixtures being added as in the previous examples. The reaction was complete in about one hour. The emulsion was cooled to room temperature and 40 g. of ammonium hydroxide added. The siloxane-acrylate co-polymer emulsion had a viscosity of 1000 cps.

Example 13

To 1350 g. of a 40% siloxane solids aqueous emulsion of a siloxane composed of 13 mol per cent of monomethylsiloxane units, 35 mol per cent of monophenylsiloxane units, 2 mol per cent of $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{SiO}_2/2$ units, 10 mole per cent of diphenylsiloxane units, and 40 mol per cent of dimethylsiloxane units there was added 970 g. of water, 10 g. of acrylic acid, 31.4 g. of an anionic surfactant and then about 40 g. of 7% sodium bicarbonate solution to adjust the pH between 5 and 6. The mixture was then heated to 85°C. and a mixture of 755 g. of ethyl acrylate, 505 g. of methyl methacrylate and 15.7 g. of acrylic acid, as well as a solution of 260 g. of water and 5 g. of potassium persulphate was added as in the previous examples. The reaction was complete in about one hour. The siloxane-acrylate co-polymer emulsion was cooled to room temperature and then 40 g. of ammonium hydroxide added.

Example 14

To 1000 g. of an aqueous emulsion of a siloxane composed of 97 mol per cent of dimethylsiloxane units and 3 mol per cent of methylvinylsiloxane units, there being about 30% of siloxane solids in the emulsion, there was added 20 g. of an anionic surfactant. The mixture was heated to 85°C. and then 300 g. of methyl methacrylate and 100 g. of a 3% hydrogen peroxide solution added. The acrylate and peroxide were added in the manner employed for adding the acrylate and persulphate of the previous

examples. The reaction was complete in about one hour, the product being an emulsion of the siloxane-acrylate copolymer.

Example 15

When 465 g. of an aqueous emulsion of a siloxane composed of 30 mol per cent of methylethylsiloxane units, 10 mol per cent of methylallylsiloxane units, 5 mole per cent of monocyclohexylsiloxane units, 40 mol per cent of monomethylsiloxane units and 15 mol per cent of monophenylsiloxane units, there being about 30% of siloxane solids in the emulsion, was mixed and reacted with 30 g. of butyl acrylate, 30 g. of methyl methacrylate and 5 g. of azobisisobutyronitrile, employing the procedure of the preceding examples, an emulsion of the siloxane-acrylate co-polymer was obtained.

Example 16

When 100 g. of an aqueous emulsion of a siloxane composed of 50 mol per cent of dimethylsiloxane units, 10 mol per cent of octadecylmethylsiloxane units, 10 mol per cent of methylvinylsiloxane units, 10 mol per cent of bromophenylmethylsiloxane units, 10 mol per cent of monobenzylsiloxane units and 10 mol per cent of monovinylsiloxane units, there being about 10% siloxane of solids in the emulsion, was mixed and reacted with 10 g. of vinyl acrylate, 80 g. of ethyl methacrylate and 3.5 g. of benzoyl peroxide, employing the procedure of the preceding examples, an emulsion of the siloxane-acrylate co-polymer was obtained.

Example 17

When the procedure of Example 16 was repeated except that the siloxane employed was composed of 40 mol per cent of dimethylsiloxane units, 5 mol per cent of phenylmethylsiloxane units, 5 mol per cent of tolylmethylsiloxane units, 15 mol per cent of monomethylsiloxane units, 30 mol per cent of monovinylsiloxane units and 5 mol per cent of $\text{C}_2\text{H}_5\text{SCH}_2\text{CH}_2\text{SiO}_2/2$ units, and the peroxide employed was tertiary butyl hydroperoxide, similar results were obtained.

Example 18

When 165 g. of an aqueous emulsion of a siloxane composed of 40 mol per cent of dimethylsiloxane units, 10 mol per cent of 3,3,3-trifluoropropylmethylsiloxane units, 5 mole per cent of monovinylsiloxane units, 10 mol per cent of monophenylsiloxane units, 10 mol per cent of 3,3,3-trifluoropropylsiloxane units and 25 mol per cent of monomethylsiloxane units, there being about 30% of siloxane solids in the emulsion, was mixed and reacted with 200 g. of methyl methacrylate, 135 g. of perfluoroethyl acrylate and 2 g. of ammonium persulphate, employing the procedure of the preceding examples, an

emulsion of the siloxane-acrylate co-polymer was obtained.

WHAT WE CLAIM IS:—

1. A process for preparing a polysiloxane-organic co-polymer which comprises (1) preparing an emulsion of a polysiloxane containing a vinylidene substituent, (2) adding at least one organic olefinically unsaturated monomer to the polysiloxane emulsion, and (3) thereafter co-polymerising the polysiloxane and the organic monomer.

2. A modification of the process claimed in claim 1, wherein the organic monomer is emulsified together with the polysiloxane.

3. A process as claimed in claim 1 or 2, wherein a catalyst is employed for the co-polymerisation of the polysiloxane and the organic monomer.

4. A process as claimed in claim 3, wherein the catalyst is a free radical generating catalyst.

5. A process as claimed in any one of the preceding claims wherein, in addition to the vinylidene substituent, the polysiloxane also contains substituents selected from

methyl, ethyl, vinyl, phenyl and 3,3,3-trifluoropropyl radicals.

6. A process as claimed in any one of the preceding claims wherein the organic monomer is selected from the acrylates, styrene, vinyl acetate, vinyl chloride and acrylonitrile.

7. A process as claimed in any one of the preceding claims wherein the preparation of the emulsion of a polysiloxane containing a substituent comprising an ethylenic double bond is carried out by emulsion polymerisation of an alkoxysilane employing ammonium hydroxide as the catalyst.

8. A process as claimed in claim 1 or 2 and with reference to any of the examples.

9. Polysiloxane-organic co-polymers when prepared by the process claimed in any one of the preceding claims.

ELKINGTON & FIFE,
Chartered Patent Agents,
High Holborn House,
52/54, High Holborn,
London, W.C.1,
Agents for the Applicants.